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Carbon–Silicon and Carbon–Carbon Bond Formation by Elimination Reactions at Metal N-Heterocyclic Carbene Complexes**

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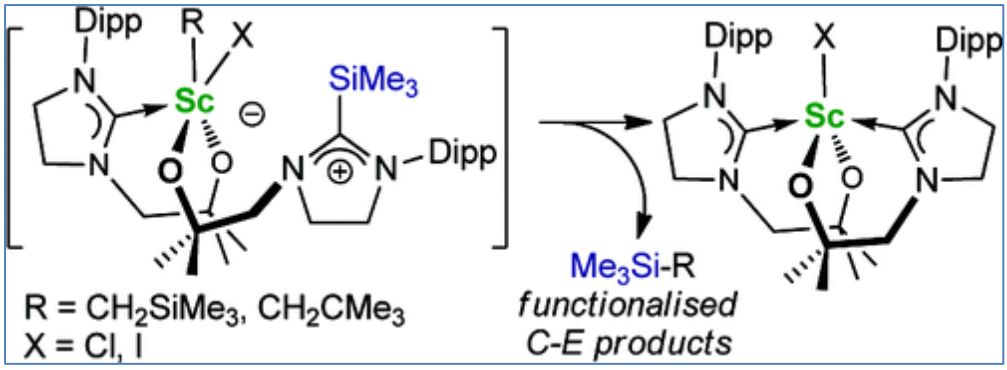
Supporting information:
Full experimental details and X-ray crystallographic data (CIFs deposited with the CCDC, codes 824248-824254 and 824414). This material is available free of charge via the Internet at www.ccdc.cam.ac.uk

Graphical abstract:



Abstract

Two functional groups can be delivered at once to organo-rare earth complexes $(L)MR_2$ and $(L)_2MR$ (M = Sc, Y; L = ({C(NDippCH$_2$CH$_2$N)}CH$_2$CMe$_2$O), Dipp = 2,6-^{i}Pr$_2$-C$_6$H$_3$; R = CH$_2$SiMe$_3$, CH$_2$CMe$_3$), *via* the addition of E-X across the metal-carbene bond to form a zwitterionic imidazolinium metal complex $(L^E)MR_2X$, where L^E = {1-EC(NDippCH$_2$CH$_2$N)}CH$_2$CMe$_2$O, E is a p-block functional group such as SiR_3, PR_2, SnR_3 and X is a halide. The 'ate' complex $(L^{Li})ScR_3$ is readily accessible, and is best described as a Li carbene adduct, {1-Li(thf)C(NDippCH$_2$CH$_2$N)}CH$_2$CMe$_2$O)Sc(CH$_2$SiMe$_3$)$_3$, since structural characterization shows the alkoxide ligand bridging the two metals and the carbene Li-bound with the shortest yet recorded Li-C bond distance. This can be converted *via* lithium halide-eliminating salt metathesis reactions to alkylated or silylated imidazolinium derivatives $(L^E)ScR_3$, E = SiMe$_3$ or CPh$_3$. All the E-functionalized imidazolinium complexes spontaneously eliminate functionalized hydrocarbyl compounds upon warming to room temperature or slightly above, forming new organic products ER, *i.e.* forming C-Si, C-P, and C-Sn bonds, and reforming the inorganic metal carbene (L)MR(X) or $(L)_2MX$ complex respectively. Warming the tris(alkyl) complexes $(L^E)MR_3$ forms organic products arising from C-C or C-Si bond formation, and appear to proceed *via* the same elimination route. Treatment of $(L)_2Sc(CH_2SiMe_3)$ with iodopentafluorobenzene results in the 'reverse sense' addition, which upon thermolysis forms the metal aryl complex $(L)_2Sc(C_6F_5)$ and releases the iodoalkane Me_3SiCH_2I, again facilitated by the reversible functionalisation of the NHC group in these tethered systems.

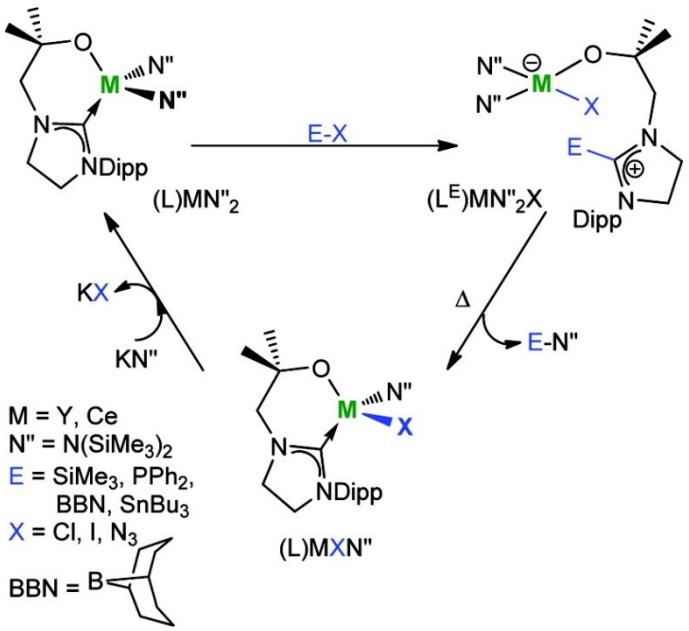
Introduction

Carbon-element bond formation reactions are important for a wide range of synthetic and catalytic transformations; their formation can be controlled and catalysed by many metal complexes from across the periodic table, *via* various reaction types.[1] In homogeneous catalysis the lanthanides and actinides are characterized by their facile bond activation reactions that proceed through a four-centered σ-bond metathesis mechanism rather than a conventional two-electron oxidative addition-reductive elimination pathway.[2] For example, the first example of methane activation was observed in the reaction between $Cp^*_2YCH_3$ (Cp* = C_5Me_5) and $^{13}CH_4$ which results in the interchange of labeled Y-$^{13}CH_3$ and unlabelled Y-$^{12}CH_3$ groups.[3] The methane interconversion reactions in these systems are non-productive because the H atom always resides in the β position in the four-centre σ-bond metathesis transition state. However, Tilley's group has demonstrated that silicon can take this β position, and used this to generate complexes capable of catalytic carbon-silicon bond formation: the reaction of CH_4 with Ph_2SiH_2 in the presence of catalytic (10 %) amounts of $Cp^*_2ScCH_3$ affords

Ph_2MeSiH and H_2 (Cp* = C_5Me_5). The reductive elimination of C-element bonds is a fundamental step in organic chemistry and homogeneous catalysis, and is generally seen for platinum group metal – based catalysts; the formation of C-C and C-Si bond is somewhat more fundamental and more difficult.[4] While other Cp^*_2LnR alkyl complexes exhibit interesting hydrocarbon chemistry such as β–carbon elimination from $Cp^*_2Sm(CH_2CMe_3)$ to form the bridging planar trimethylenemethane dianion in $\{(Cp^*)_2Sm\}_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C(CH_2)_3)$.[5] the formation of C-element bonds using early d- and f-block metal catalysts is best represented by a variety of hydroelementation reactions, in which an organolanthanide complex catalyses the controlled addition of H and a main group element functional group (amine, phosphine, thiol, alcohol) across an unsaturated C-C bond,[6] *i.e.* catalysts for the hydroamination, phosphination, alkoxylation, and silylation of alkenes. These too rely on σ-bond metathesis mechanisms to exchange the substrate and product at the end of each turnover. A range of asymmetric Michael addition reactions are probably the most well–known carbon-carbon bond forming reactions currently known for rare-earth alkoxide complexes in which the metal coordinates and activates a substrate prior to attack by a carbanion; basic lanthanum BINOL-ate derivatives were the first asymmetric catalysts for nitroaldol reactions.[7] Carbon-element bond forming reactions that take place at a σ-bound rare-earth alkyl group however are rare. Early transition metal complexes often react with N-heterocycles to lead to *ortho*-metallated complexes and Teuben's group reported that $(Cp^*)_2Y(\eta^2\text{-C,N-}NC_5H_4)$ is formed from the hydride $[(Cp^*)_2YH]_2$ by the selective metallation of pyridine.[8] The hydride also metallates other arenes. The addition of a further equivalent of pyridine forms the adduct $(Cp^*)_2Y(\eta^1\text{-2-}NC_5H_4)(NC_5H_5NC_5H_5)$ which on heating first forms the non-aromatic C-C coupled product $(Cp^*)_2Y\{\kappa^1\text{-2,2'-}NC_5H_5(2\text{-}NC_5H_4)\}$ by insertion, then eliminates hydrogen, allowing 2,2'-bipyridine to be eliminated upon quenching of the complex, or 2-alkylated pyridines to be formed if alkenes were incorporated into the mixture. Recently, Diaconescu reported similar scandium(III) chemistry in which two pyridine ligands were C-C coupled to form a ligated dearomatized bipyridine,[9] in a mechanism also proposed to occur *via* σ-bond metathesis chemistry since other oxidation states are not generally accessible for group 3 metals.[10]

We recently demonstrated that two functional groups can be delivered to an f-block metal at once by the use of a bound N-heterocyclic carbene as a reactive donor ligand.[11] A polar reagent such as a halosilane can be added across the metal carbene bond, quaternizing the imidazolinium fragment, driven by the formation of the metal-halide bond. This functions as a substitute to an oxidative addition reaction at a metal with an accessible M^n/M^{n+2} redox pair. The elimination reaction that completes the formal addition/elimination pair could be achieved by heating the complex to regenerate the metal carbene bond, releasing the carbene-bound electrophile now bound to an anion formerly coordinated to the metal. Scheme 1 shows a generic scheme for the addition of E-X (E = SiR_3, BR_2, PR_2, SnR_3; X = Cl, N_3) to (L)MN"$_2$ (M = Y, Ce; L = $\{C(NDippCH_2CH_2N)\}CH_2CMe_2O$) to

afford (L^E)MN"$_2$X (L^E = {1-EC(NDippCH$_2$CH$_2$N)}CH$_2$CMe$_2$O)MN"$_2$X , Dipp = 2,6-^{i}Pr$_2$-C$_6$H$_3$), then thermally induced elimination of E-N", and a final salt metathesis step to regenerate (L)MN"$_2$.



Scheme 1. Addition-elimination cycles of reactivity for d^0 metal carbene complexes with E-X.

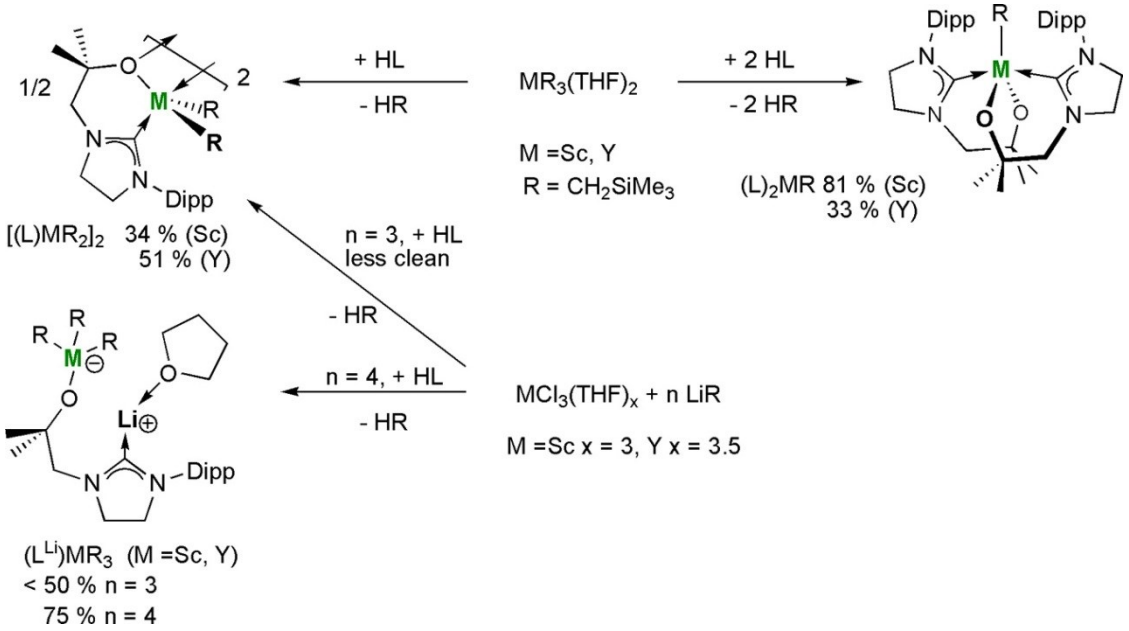
A small but increasing number of examples of non-innocent behaviour of the imidazolinium NHC unit are being reported, and these instances include reactions of early transition metal and f-block N-heterocyclic carbene complexes that are being explored for an increasing array of catalytic chemistry.[12;13] In a most recent case, a Zr^{IV} complex of a dianionic bis(aryloxide) carbene complex (L)Zr(CH$_2$Ph)(Cl) (L = CN(3,5-^{t}Bu-C$_6$H$_2$O)CH$_2$CH$_2$(3,5-^{t}Bu-C$_6$H$_2$O) has been shown to be isolable, but additional donor coordination (a thf molecule) promotes benzyl migration from the metal to the carbene carbon, representing classical Fischer-type carbene behaviour and converting the carbene C to an sp^3-hybridized carbanion, and allowing additional donation from the two NHC nitrogen atoms to the metal.[14] Mid- to high-oxidation state group 10 alkyl carbene complexes are known to suffer from decomposition *via* the reductive elimination of a monodentate NHC and alkyl group to form a C1-alkylated imidazolium salt, with concomitant release of the two electron reduced metal complex. In certain cases, this can be used for productive heterocycle functionalization.[15] In related chemistry, a Ni^{II} hydrocarbyl complex NiClPh(PPh$_3$)$_2$ reacted with a bidentate saturated imidazolium NHC ligand to ring open the NHC group *via* insertion into one N-C bond, the product presumably resulting from the intramolecular attack by the Ni-bound alkyl on the empty carbene p orbital followed by the reductive elimination of the 2-alkylimidazolinium salt.[16] Possibly the most interesting C-N bond

reactivity observed recently in nitrogen heterocycles relates to the C-C coupling, ring size reduction and dearomatization of imidazole- and NHC-supported Re-bound pyridines when treated with protons or methyl triflate.[13]

Aware of the absence of two-electron redox reactivity for the rare earth metals, the clean and reversible amido-functionalization chemistry elucidated in Scheme 1, and the potentially useful hydrocarbon reactivity that low-coordinate f-block complexes show, we have sought to extend the addition-elimination reactivity to alkyl-lanthanide complexes. Herein, we show how this strategy can be used to effect carbon-silicon and carbon-carbon bond forming reactions at organo-rare earth carbene complexes, as well as the derivatization of f-block alkyls with heteroatom functional groups such as stannanes or phosphines. We also demonstrate a new route to perfluoroaryl-rare earth complexes that avoids the use of mercury reagents.

Results

Syntheses of mono and bis(carbene) metal alkyl complexes



Scheme 2. Syntheses of rare earth metal carbene alkyl complexes.

Complexes containing the σ-alkyl ligands neosilyl (CH_2SiMe_3) and neopentyl (Np = CH_2CMe_3) were chosen as targets with which to study the NHC-labilization chemistry; both mono and bis(ligand)

compounds of the rare earth Y^{III} and Sc^{III} cations are accessible using these anions. The mono(carbene) alkyl complexes $[(L)MR_2]_2$ (M = Sc or Y, R = CH_2SiMe_3) can be made readily from the thermally sensitive tris(alkyl) complexes by a protonolysis reaction between $MR_3(thf)_2$ and HL in hexanes or hexanes/thf at 0 °C, and isolated in 62 % (Sc) and 51 % (Y) yield. The preparation of the same complexes from an *in situ* reaction of $MCl_3(thf)_n$ (n = 3 Sc, n = 3.5 Y) and three equivalents of LiR is less clean since the 'ate' complex $(L^{Li})MR_3$ forms more readily than the neutral complex, so extra purification steps are required.[17] The 'ate' complex can be made specifically from treatment of $MCl_3(thf)_n$ with four equivalents of LiR and one equivalent of HL, Scheme 2. The alkyl complexes $[(L)MR_2]_2$ are dimeric at least in the solid state show much lower air- and thermal stability than the heterobimetallic 'ate' complexes, and the Sc complexes are much more readily isolated than the yttrium complexes, presumably due to the greater degree of steric protection afforded by the ligands to Sc. The three complexes $[(L)ScR_2]_2$, $[(L)YR_2]_2$, and $(L^{Li})MR_3$ have all been structurally characterized by single crystal X-ray diffraction techniques. The structures are discussed below.

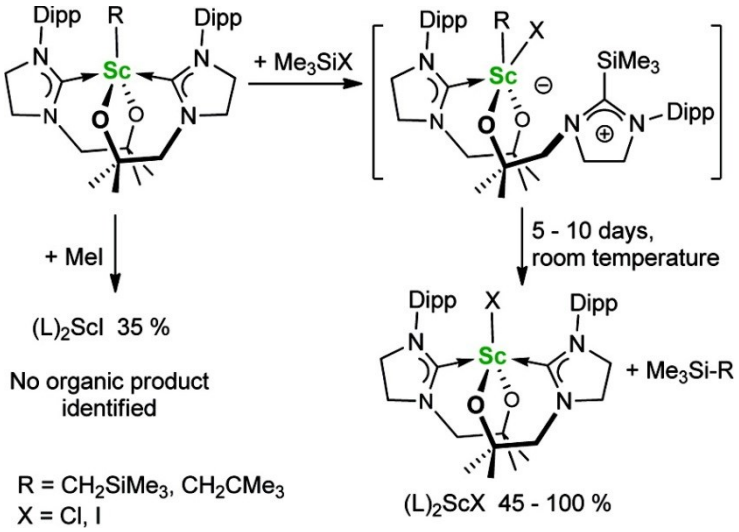
The bis(carbene) alkyls $(L)_2MR$ (M = Sc or Y, R = CH_2SiMe_3) can also be made from the tris(alkyl) complexes $MR_3(thf)_2$ by treatment with two equivalents of the proligand HL in hexanes (Sc) or toluene (Y) at 0 °C. All reaction mixtures were stirred at room temperature before the volatiles were removed *in vacuo* to yield the final products in 33 % ($(L)_2YR$) and 81 % ($(L)_2ScR$) yield, Scheme 1. These complexes are significantly more thermally stable than the mono(L) complexes, and have thus been used for the majority of reactivity studies described below. The complex $(L)_2ScR$ can be heated to 80 °C in C_6D_6 without noticeable signs of decomposition. The ^1H NMR spectra of all of the bis(ligand) alkyl compounds were indicative of a rigid molecular structure in solution at room temperature. For example, in $(L)_2ScR$ four doublets define the $CH\underline{Me}_2$ protons of the Dipp groups and two singlets for the CMe_2 alkoxy arm protons. The $C\underline{H}_2SiMe_3$ alkyl resonances show geminal coupling ($^2J_{HH}$ = 11 Hz) and appear as two doublets, implying the restricted rotation of the scandium alkyl Sc-CH_2SiMe_3 bond. In the analogous $(L)_2YR$, a doublet of doublets represents the $C\underline{H}_2SiMe_3$ protons due to the coupling to yttrium ($^1J_{YH}$ = 3 Hz) in addition to the geminal coupling of the protons ($^2J_{HH}$ = 11 Hz). The synthesis and characterization of the neopentyl complex $(L)_2ScR$ (R = CH_2CMe_3) has also been carried out successfully in 47 % yield; details are included in the supplementary information.

Addition/elimination reactions of metal carbene alkyl complexes to form carbon-silicon and carbon-carbon bonds

The reactions of these alkyl complexes with reagents that can add across the metal carbene bond allows for the formation of carbon-heteroatom bonds, and for the study of C-C and C-Si bond

formation from an organolanthanide complex. The reaction chemistry of the bis(ligand) scandium complex has been studied in greatest detail due to the superior thermal stability of the complex, but additional NMR tube - scale reactions of the yttrium analogue, and mono(carbene) analogues have been carried out in a number of cases to ensure the generality of the procedures; these are included in the SI.

Reactions of $(L)_2Sc(CH_2SiMe_3)$ and $(L)_2Sc(CH_2CMe_3)$ with halosilanes and haloalkanes: C-Si bond formation

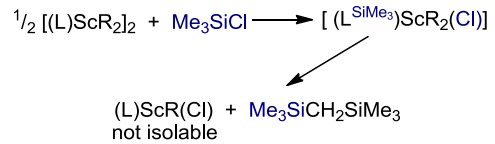


Scheme 3. Formation of C-Si bonds from addition of halosilanes to d^0 metal carbene complexes

Treatment of the bis(ligand) Sc neosilyl or neopentyl complex $(L)_2ScR$ with one equivalent of trimethylsilyl chloride or iodide in benzene results in the formation of a clear, colorless solution which slowly (over five days for R = CH_2SiMe_3 and ten days for R = CH_2CMe_3) at room temperature react to form a clean mixture of $(L)_2ScCl$ and the product of C-Si bond formation, $Me_3SiCH_2SiMe_3$ or $Me_3SiCH_2CMe_3$ respectively, in each case, Scheme 3. Here, and in the following cases, the organic product has been identified by NMR spectroscopies and/or mass spectrometry, and by comparison with spectra of genuine samples of the organic product. At the end of the five day reaction period, an unstirred reaction between $(L)_2ScR$ (R = CH_2SiMe_3) and Me_3SiCl had deposited single crystals of the Sc product $(L)_2ScCl$ which were suitable for a single crystal structural analysis; details are given below.

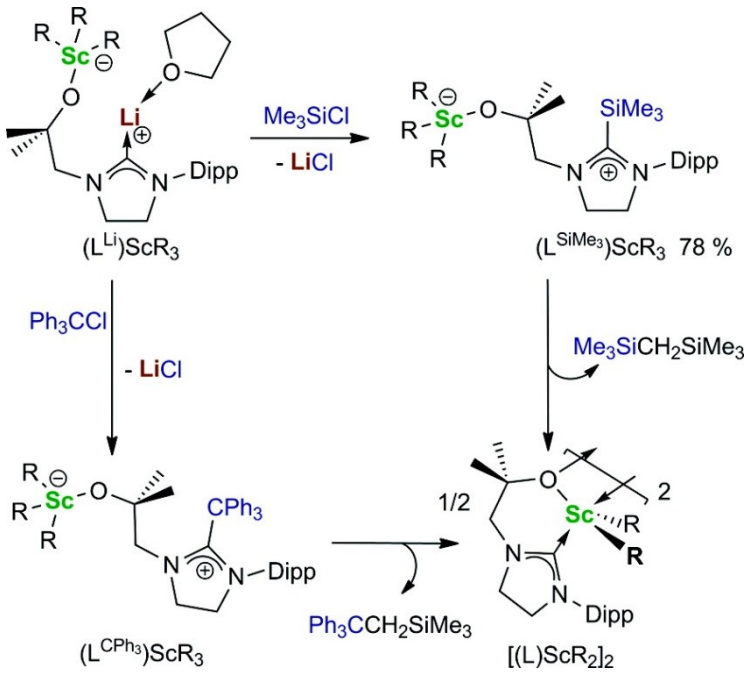
In an effort to extend C-Si bond formation to C-C bond formation, we carried out the reactions of $(L)_2MR$ (M = Sc or Y, R = CH_2SiMe_3 or CH_2CMe_3) with a number of alkyl halides (MeI, ^{i}PrCl, ^{i}PrI, ^{t}BuI, Ph_3CCl, CH_2CHCH_2Cl, BnBr, Me_3SiCH_2Cl) and aryl halides (PhCl, PhI, C_6F_5I). In a typical reaction, an equimolar quantity of each reagent was combined in a J-Young Teflon valve NMR tube in C_6D_6 (0.5 mL). The ^{1}H NMR spectrum was recorded immediately and then after the reaction mixture had been heated to 80 ºC for 16 h. In all but the tube containing $(L)_2Sc(CH_2SiMe_3)$ and MeI or C_6F_5I (see below), no reaction had occurred. In the reaction with MeI no reaction was observed until the mixture was heated; after two hours at 80 ºC the scandium iodide, inorganic product $(L)_2ScI$ was isolated in 35 % yield, but no C-C bonded organic product $H_3C\text{-}CH_2SiMe_3$ was observed, suggesting decomposition of the CH_3I has occurred. The same outcome was observed in the presence or absence of daylight (where MeI is known to liberate free I_2) and MeI is thermally stable up to 270 ºC. When the reaction was carried out with an excess of MeI, the solution became red-brown in color due to the formation of I_2. No haloalkane Me_3SiCH_2I was observed in the reaction mixture, a byproduct which might be expected from a reaction with I_2. X-ray quality single crystals of $(L)_2ScI$ were grown from a toluene solution of this reaction mixture at room temperature, confirming its structure, see below and the SI for further details of the molecular structure. This observation supports the assignment of a general addition/elimination mechanism for the reactions. In the reaction with C_6F_5I, a formally reverse sense addition across the M-$C_{carbene}$ bond and subsequent C-I bond formation has occurred, *i.e.* $(L)_2Sc(C_6F_5)$ and Me_3SiCH_2I are the products; this is discussed below.

Reaction of $[(L)Sc(CH_2SiMe_3)_2]_2$ with halosilanes and haloalkanes: C-Si and C-C bond formation



The mono(ligand) neosilyl complex $[(L)ScR_2]_2$ (R = CH_2SiMe_3) reacts much more quickly than the bis(ligand) complex with one equivalent of trimethylsilyl chloride in benzene to form a clear, colorless solution (over 3 h at 25 ºC) which contains the product of C-Si bond formation $Me_3SiCH_2SiMe_3$, eq. 1. As before, the most reasonable mechanism for this reactivity involves the initial addition across the M-$C_{carbene}$ bond to form the quaternized NHC complex $(L^{SiMe3})ScR_2(Cl)$, which decomposes at room temperature cleanly eliminating $Me_3SiCH_2SiMe_3$. If this mechanism is occurring then the scandium-containing byproduct should be (L)ScR(Cl), but it is not observed in the

byproducts. In the analogous amide chemistry the product (L)MN"Cl was usually observed to redistribute ligands to form equimolar (L)MN"$_2$ and (L)MCl$_2$. Here, neither (L)ScR(Cl) nor [(L)ScR$_2$]$_2$ is found in solution, suggesting that the sterically unsaturated (L)ScR(Cl) product could be formed but has decomposed.



Scheme 4. Formation of C-Si and C-C bonds from the addition of group 14 halides to [(L)MR$_2$]$_2$.

The heterobimetallic ScLi compound (L^{Li})ScR$_3$ allows another route to the introduction of a functional group *via* metathetical displacement of the lithium cation. Thus treatment with either trimethylsilyl chloride or triphenylmethyl chloride at room temperature affords a colorless precipitate of lithium chloride and the 2-silylated or 2-alkylated imidazolinium scandium complex (L ^{SiMe3})ScR$_3$ and (L^{CPh3})ScR$_3$ respectively after one or two hours, Scheme 4. If the mixture is kept at 0 °C, the silylated imidazolinium complex (L ^{SiMe3})ScR$_3$ is isolable as a colorless powder in 78 % yield, and has been fully characterized. This reaction effectively generates the intermediate in the addition-elimination reactivity scheme which could not be isolated when the mono(ligand) alkyl complexes were treated with Me$_3$SiCl. The increased stability may arise from the greater steric protection of the scandium centre by the presence of three CH$_2$SiMe$_3$ ligands rather than two neosilyl and one chloride ligand, which has a lesser steric demand.[18] Upon warming to room temperature the isolated powder of (L^{SiMe3})ScR$_3$ decomposes in the solid state, but if redissolved in toluene, it cleanly undergoes elimination chemistry: by integration of the ^{1}H NMR spectrum, approximately 0.9 equivalents of the

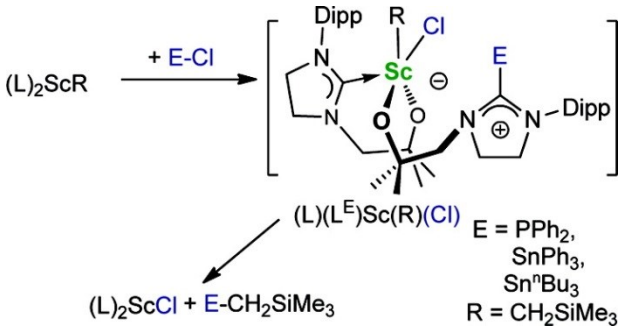
anticipated (L)ScR_2 was formed. A small amount of $(L)_2ScR$ (~0.1 equivalents) was also observed, presumably as a result of ligand redistribution to this more stable product. Heating a toluene solution of (L^{CPh3})ScR_3 results similarly in the straightforward spontaneous thermal elimination of Ph_3C-CH_2SiMe_3 to regenerate (L)ScR_2. This represents a new way to achieve carbon-carbon bond formation from a rare earth complex. From the reaction mixture that formed (L)ScR_2 and Ph_3C-CH_2SiMe_3, single crystals of the Sc alkyl complex were grown of sufficient quality for a single crystal X-ray structural determination. The structure is discussed below.

The C-Cl bond strength in trityl chloride Ph_3C-Cl is very weak, estimated as 280 $kJmol^{-1}$,[19] rendering it an easy substrate with which to demonstrate the C-C bond formation reaction. No evidence for the formation of Gomberg's hydrocarbon dimer was found by spectroscopy, confirming the absence of any competing homolytic Ph_3C-X cleavage chemistry. This observation again supports the assignment of a general addition/elimination mechanism for the reactions. No reaction was observed between (L^{Li})ScR_3 and simpler alkyl or aryl halides such as ^{i}PrCl, ^{i}PrI, ^{t}BuI, $PhCH_2Br$, PhCl or PhI.

Addition/elimination reactions of metal carbene alkyl complexes to form other carbon-heteroatom bonds

We also previously communicated reactions of the amido complexes with halophosphines, boranes and stannanes, which resulted in the formation of new N-element bonds. It is now possible to extend these reactions to the formation of carbon-heteroatom bonds.

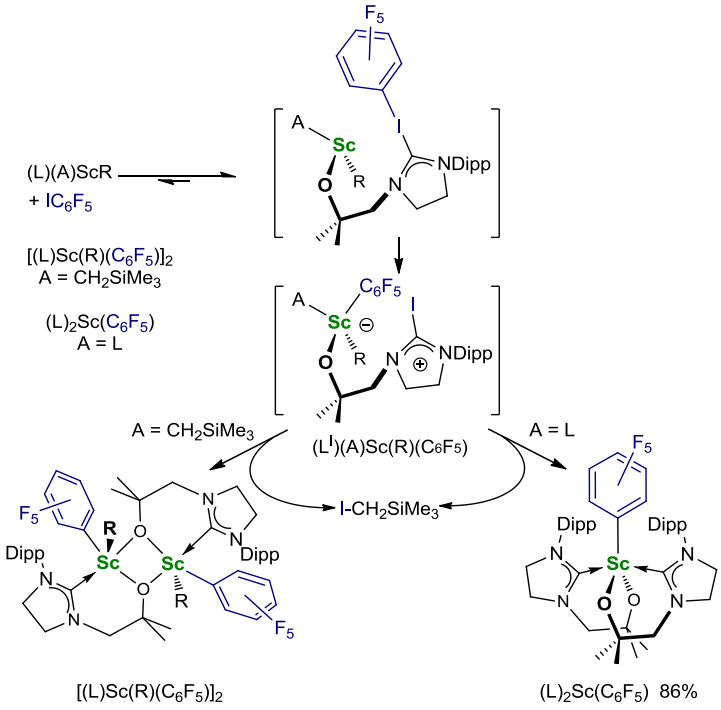
Halophosphines and stannanes: C-P and C-Sn bond formation



Scheme 5. Formation of C-heteroatom bonds from the addition of halogenated p-block reagents to $(L)_2ScR$ (R = CH_2SiMe_3).

The reaction of (L)ScR_2 (R = CH_2SiMe_3) at room temperature in C_6D_6 with one equivalent of $^tBu_3SnCl$, Ph_3SnCl or Ph_2PCl resulted in C-Sn and C-P bond formation to yield $^tBu_3SnCH_2SiMe_3$, $Ph_3SnCH_2SiMe_3$ and $Ph_2PCH_2SiMe_3$ respectively with the generation of $(L)_2ScCl$. Scheme 5 shows the general reaction sequence to make tin and phosphorus alkyls alongside the conversion of $(L)_2ScR$ into $(L)_2ScCl$. Again no intermediate imidazolinium complexes are observed by NMR spectroscopy, despite the reaction to form the P-C bond proceeding over the course of five days, suggesting the addition across the metal-carbene bond is the rate limiting step. A surprising difference in the reaction time was observed in the tin chemistry; the formation of $^nBu_3SnCH_2SiMe_3$ proceeds quantitatively over 17 hours, but the formation of $Ph_3SnCH_2SiMe_3$ take up to five days to reach completion. The $^nBu_3SnCH_2SiMe_3$ product was identified by both EI-MS (*m/z* = 363.1 $[M\text{-}Me]^+$) and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance for the methylene ^nBu carbons of $^nBu_3SnCH_2SiMe_3$ occurs at 10.7 ppm and coupling to the NMR active ^{119}Sn and ^{117}Sn isotopes was visible as tin satellites ($^2J_{119SnC}$ = 162 Hz, $^2J_{117SnC}$ = 155 Hz).

Perfluoroaryl iodides: C-I bond formation



In contrast to the addition of group 14 and 15 halides, and as mentioned above, the reaction of $[(L)ScR_2]_2$ (R = CH_2SiMe_3) with C_6F_5I proceeds instantly to afford the product arising from the

addition in the reverse sense, *i.e.* the carbene forms the 2-iodoimidazolinium salt and a metal aryl bond is formed. The two products isolated from the reaction are the alkyl halide Me_3SiCH_2I and $(L)Sc(R)(C_6F_5)$ which crystallizes as an alkoxide bridged dimer, eq. 2. The analogous reaction between $(L)_2ScR$ and C_6F_5I was found to proceed equally cleanly, with both $(L)_2Sc(C_6F_5)$ (isolated in 86 % yield) and Me_3SiCH_2I identified as the products. X-ray quality single crystals of $[(L)Sc(R)(C_6F_5)]_2$ and $(L)_2Sc(C_6F_5)$ were grown from toluene solution of the reaction mixtures at -20 ºC and at room temperature respectively. The molecular structure of $[(L)Sc(R)(C_6F_5)]_2$ is described in the SI, while that of monomeric $(L)_2Sc(C_6F_5)$ is shown in Figure 1e).

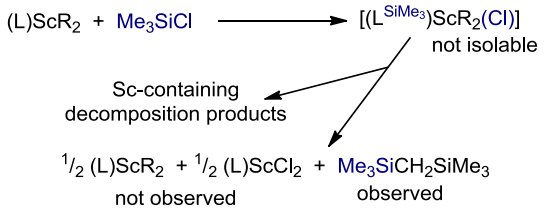
Discussion

It is proposed that as before (Scheme 1), the mechanism which leads to the elimination of organic products with new carbon-element bonds arises from the initial addition of the E-X reagent across the $M\text{-}C_{carbene}$ bond in a heterolytic fashion to form a quaternized imidazolinium complex. For example, $(L)_2ScR$ reacts with Me_3SiCl to form $(L^{SiMe3})(L)ScR(Cl)$, $\{1\text{-}Me_3SiC(NDippCH_2CH_2N)\}CH_2CMe_2O)(C(NDippCH_2CH_2N)\}CH_2CMe_2O)Sc(CH_2SiMe_3)Cl$ initially. The addition reaction appears to be driven by the formation of a strong M-X bond (Sc-Cl: 464 $kJmol^{-1}$ in $ScCl_3$; 331 $kJmol^{-1}$ for the diatomic ScCl, Y-Cl: 523 ± 84 $kJmol^{-1}$ for diatomic YCl) and the use of a polar substrate. Upon warming to room temperature this 'ate'-like complex cleanly eliminates $Me_3SiCH_2SiMe_3$, reforming a metal carbene complex; in this example $(L)_2ScCl$.[11] In the bis(ligand) complex reactions no inorganic products other than $(L)_2ScX$ are isolated and we assume that only one of the two NHC groups is functionalized by the addition reaction, since the functionalization of two would place a large negative change on the Sc centre which seems unlikely. The bis(ligand) complex $(L)_2ScCl$ is readily reconverted back to the alkyl $(L)_2ScR$ starting materials, but the mono(ligand) chemistry is insufficiently stable to allow the metal complex to be recycled in this manner. This parallels the increased thermal stability of $(L)_2ScR$ with respect to $[(L)ScR_2]_2$. The tris(alkyl) complex $(L^{CPh3})ScR_3$ is however sufficiently thermally stable that it can be isolated at low temperature in the solid state, but if redissolved in toluene, it cleanly undergoes elimination chemistry to form $Me_3Si\text{-}CH_2SiMe_3$ as anticipated, and $[(L)ScR_2]_2$. The isolation of both of these mono(ligand) products suggests that steric congestion is the main factor allowing their isolation. The straightforward spontaneous thermal elimination of $Ph_3C\text{-}CH_2SiMe_3$ from $(L^{CPh3})ScR_3$ to regenerate $[(L)ScR_2]_2$ is a new way to achieve carbon-carbon bond formation from a rare earth complex. This reactivity may be likened to that of 'frustrated Lewis pairs', in which a Lewis acid and Lewis base too bulky to react with each other, *e.g.* a bulky phosphine PR_3 in combination with strongly electrophilic $B(R)(C_6F_5)_2$ can react to cleave H_2 (or other small molecules) in a heterolytic manner affording $[HPR_3][HBR_3]$.[20] In contrast to the amido chemistry, in the Ln-alkyl systems the intermediates are not

sufficiently stable to allow the isolation of single crystals which would provide structural confirmation of the intermediates. Another related possibility for the mechanism is suggested by consideration of the unusual stabilizing capabilities of the N-heterocyclic carbene. It is known that the coordination of small molecules to an NHC can reduce the strength of the adjacent bonds by a surprisingly large amount; the B-H BDE of an NHC-coordinated BH_3 molecule H_3B-C(NDippCH)$_2$ is lowered by approximately 125 kJmol^{-1} compared with the BH_3 B-H bond.[21] Thus NHC-borane complexes are an emerging class of reagents for a variety of reduction reactions.[22] We have shown before that neutral Lewis acids such as boranes can compete with rare-earth metal centers for the NHC group in these bidentate ligands,[23] and it seems reasonable that a labilized NHC group in a mono- or bis(ligand) complex might have a similar effect on one of these substrates.

The formation of an organic product with a new C-Si bond is observed for scandium silylalkyl and scandium alkyl complexes, and also in the reaction of $(L)_2YR$ with Me_3SiCl, showing the generality of the reaction. However, the addition of a range of alkyl halides, even those with very weak carbon-halogen bonds (such as Ph_3CCl), in an attempt to form carbon-carbon bonded products was not successful in this respect. Low yields of the iodide $(L)_2ScI$ are formed from reactions of $(L)_2ScR$ with methyl iodide, but only under conditions at which the MeI reagent can decompose, suggesting a simple radical attack, and no reaction is observed between $(L)_2ScR$ and PhI. The C-I bond strength in Me-I is 239 kJmol^{-1}, that in Ph-I is 281 kJmol^{-1}.[24;25] Alkyl halides such as *tert*-butyl chloride have previously been shown to act as a single electron oxidant towards Ln^{II} organometallics to form a Ln^{III} halide, but there is no reason that any direct Ln^{III} - alkyl halide reactivity might be anticipated.[26]

In the case of the mono(ligand) product, the instability of the metal product formed from the elimination step hampers the development of this system. We previously observed in the $(L)MN''_2$ systems that the mono(ligand) products formed after elimination of the organic amine, i.e. (L)LnN"Cl, were susceptible to ligand redistribution reactions, forming a 50:50 mixture of $(L)MN''_2$ and $(L)MX_2$.



If this was the case here, one would anticipate $[(L)ScR_2]_2$ and $(L)ScCl_2$ although maybe only the former is isolable. It appears here that the mono(alkyl) complex (L)ScR(Cl) is insufficiently unstable

to undergo any ligand distribution process before it decomposes, eq. 3, with the result that we have focused further C-heteroatom bond forming reactivity studies on the bis(ligand) complexes.

The heterobimetallic alkyl complex (L^{Li})ScR_3 in which the carbene binds to the lithium cation allows a straightforward carbene-C-alkylation to be carried out, and the quaternized intermediate, (L^{CPh3})ScR_3 with no coordinated halide allows the formation of a C-C bonded organic product to be formed smoothly, without any decomposition of the final inorganic product since the dialkyl scandium complex (L)ScR_2 is also thermally stable. This represents a new type of C-C bond forming reaction, and one of particular potential use to a metal complex with no access to two-electron reductive elimination chemistry.

The robust bis(ligand)Sc framework has allowed the study of the formation of C-heteroatom bonds from the addition of p-block halides to the rare earth alkyl $(L)_2ScR$, and the polarity of the main group halide bond makes these reactions straightforward and high yielding for the formation of C-P and C-Sn bonds. The Sn-Cl bond strength is relatively high at 425 ± 17 kJmol^{-1} in Me_3Sn–Cl,[27] but the polarity and formation of the strong Sc-Cl bond presumably drives the reaction. The use of two different tin reagents with very different sizes provides further information since the quantitative formation of $^{n}Bu_3SnCH_2SiMe_3$ takes 17 hours, but that of $Ph_3SnCH_2SiMe_3$ take up to five days. This must primarily be due to the differences in steric congestion that results in a slow addition of the triphenyl tin reagent. The Sn-Cl bond strength is high (for example, 425 ± 17 kJmol^{-1} in Me_3SnCl, 439 kJmol^{-1} in $^{n}Bu_3SnCl$ and 350 ± 8 kJmol^{-1} for the diatomic Sn-Cl)[28] but the polarity of the bond and the formation of a strong Sc-Cl bond (464 kJmol^{-1} in $ScCl_3$ and 331 kJmol^{-1} for the diatomic Sc-Cl)[28;29] is presumed to facilitate the reaction.

Precedent for the reverse addition of C_6F_5I to form the iodoimidazolinium intermediate (which is not directly observed) has been previously set. The free carbene IAd (IAd = C{N(Ad)CHCHN(Ad)}, Ad = 1-adamantyl) reacts in thf with C_6F_5I to give the reverse ylid, 2- C_6F_5-I-C{N(Ad)CHCHN(Ad)}, *i.e.* a halonium methylide ylid, a zwitterion where a positive charge is formally centered on the N-heterocyclic ring and a negative charge is on the iodine atom, which exists in an equilibrium in solution with the free carbene and C_6F_5I. The adduct reportedly underwent some decomposition in solution at room temperature over several hours, suggesting that C-I bond cleavage may occur. The complex is stable in the solid state, although the solutions were reported to decompose over a period of hours to release pentafluorobenzene and the 2-iodo-imidazolium ion, suggesting that either carbon-iodine bond can be cleaved.[30] It is interesting to compare the C-I BDE value[24] of 277 kJmol^{-1} for C_6F_5-I with that for C_6H_5-I (281 kJmol^{-1}) which was not reactive for this chemistry. The simple 2-iodo-imidazolinium salt [2-I-C$(NAdCH)_2$][I] can also be prepared by treatment of the free carbene IAd with I_2,[30] and [1-I-C$(NEtCH)_2$]I was reported to be formed from the reaction of molybdenum or chromium carbonyl complexes [M(1-C$(NEtCH)_2$)$(CO)_5$] (M = Mo or Cr) in chloroform with iodine.[31]

Stack has also the first example of reductive elimination of $C_{carbene}$-halogen bonds from $IPrCu^{III}$ halide complexes (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) to form the 1,3-bis(2,6-diisopropylphenyl)-2-chloroimidazolium cation.[32] The formation of the iodoalkane Me_3SiCH_2I associated with the formation of the ScC_6F_5 containing complexes by elimination from the Sc-R and imidazolinium-I fragments mirrors the reductive elimination of MeI from Pt^{IV} complexes which has been previously reported.[33]

Complexes containing a rare earth metal-C_6F_5 group have previously been made *via* a few distinct reactions. The reaction of elemental Yb or Eu with $HgPhC_6F_5$,[34,35] affords the Ln^{II}-C_6F_5 unit. An unusual σ-bond metathesis reaction involving either C-F or C-Si bond cleavage occurs with bis(cyclopentadienyl) cerium and samarium hydrides: The former reacts with C_6F_6 to afford $Cp^t_2Ce(C_6F_5)$ ($Cp^t = C_5{}^tBu_3H_2$);[36] the latter reacts with $C_6F_5SiH_3$ to afford $[Cp^*_2Sm(C_6F_5)]_2$ ($Cp^* = C_5Me_5$).[37] The decomposition (*via* C_6F_5 transfer to the metal) of a sterically unencumbered cationic scandium β-diketiminato complex $[Sc(Me)\{(Ar)NC(Me)CHC(Me)N(Ar)\}][MeB(C_6F_5)_3]$ affords $[Sc(C_6F_5)\{(Ar)NC(Me)CHC(Me)N(Ar)\}][Me_2B(C_6F_5)]$ (Ar = 2,6-^{i}Pr-C_6H_3).[38] Finally, the protonolysis reaction of the chiral metallacycle $Ce(\{1,2,4\text{-}^tBu\}_3C_5H_2)(\{1,2\text{-}^tBu\text{-}4\text{-}CMe_2CH_2\}C_5H_2)$ with C_6F_5H forms $Ce(\{1,2,4\text{-}^tBu\}_3C_5H_2)_2(C_6F_5)$.[36] There are also a limited number of transition metal NHC-containing complexes with a M- C_6F_5 bond that have been formed by oxidative addition of C_6F_5X (X = F, CF_3,C_6F_5),[39;40] as in the case of *trans*-$(L)_2Ni(F)(C_6F_5)$ (L = 1-C($N^iPrCH)_2$)[39] or by simple substitution reactions, as for $(L)Au(C_6F_5)$ (L = 1-$C(MeNCH)_2$).[41] Thus the iodoarene addition across the M-NHC bond straightforward reaction offers a new atom economic, and non-toxic method to introduce a fluoroaryl group.

X-ray structures of the complexes

From the reactions described above, single crystals of, $[(L)YR_2]_2$, $(L^{Li})ScR_3$, $(L)_2ScR$, $(L)_2ScCl$, $(L)_2ScI$, $(L)_2Sc(C_6F_5)$ and $[(L)Sc(R)(C_6F_5)]_2$ were grown and the molecular structure determined by X-ray diffraction. The structures of $[(L)ScR_2]_2$, $(L^{Li})ScR_3$, $(L)_2ScR$, $(L)_2ScCl$, and $(L)_2Sc(C_6F_5)$ are shown below in Figure 1, a) – e) respectively, with selected metrical data collected in Table 1. The structures of $[(L)YR_2]_2$, $(L)_2ScI$ and $[(L)Sc(R)(C_6F_5)]_2$ are discussed in the supplementary information.

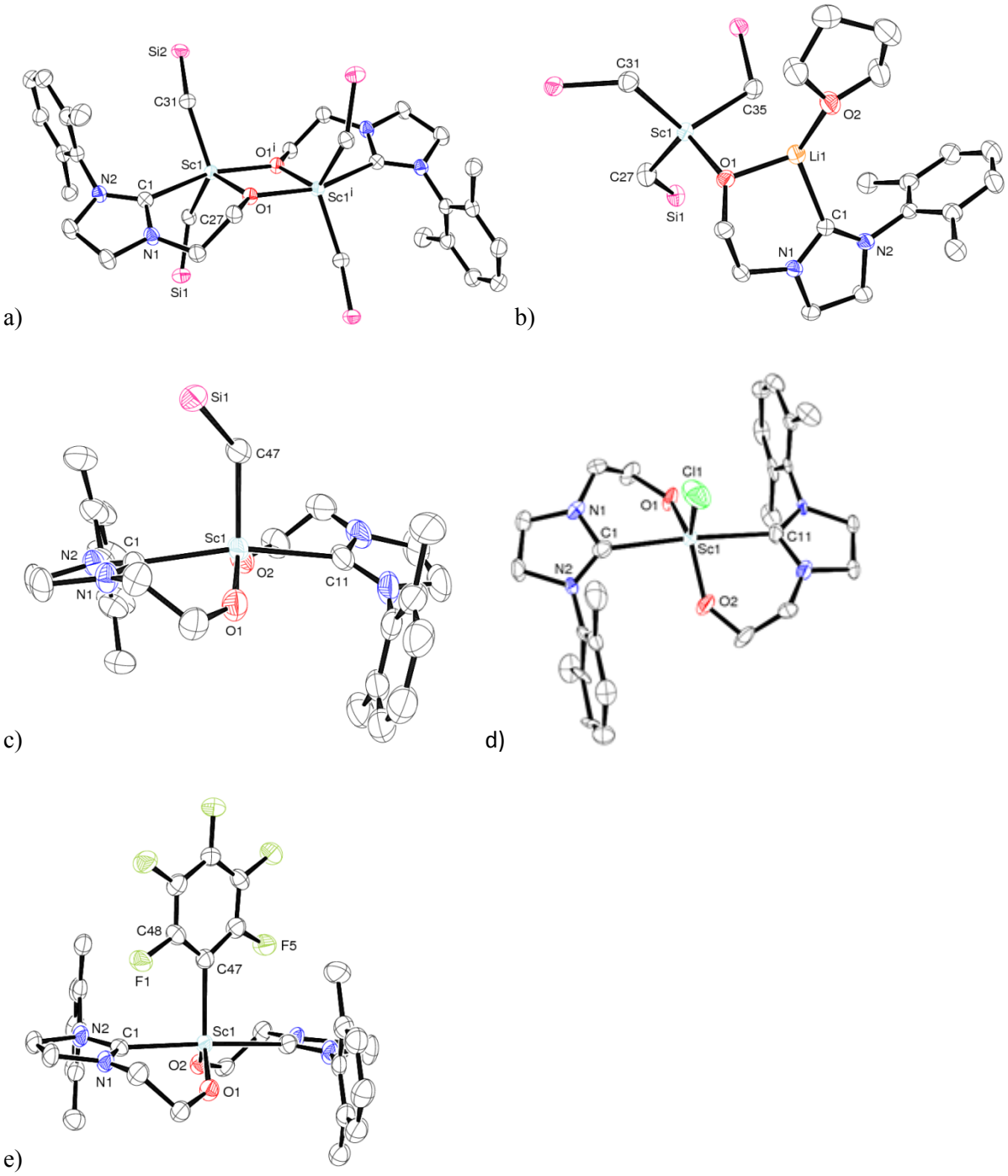


Figure 1. Thermal displacement drawings (50% probability ellipsoids) of the molecular structures of a) $[(L)ScR_2]_2$, b) $(L^{Li})ScR_3$, c) $(L)_2ScR$, d) $(L)_2ScCl$, and e) $(L)_2Sc(C_6F_5)$. Methyl groups, H atoms and lattice solvent molecules omitted for clarity.

	$[(L)ScR_2]_2$	$(L^{Li})ScR_3$	$(L)_2ScR$	$(L)_2ScCl$	$(L)_2Sc(C_6F_5)$
M-$C_{carbene}$	2.4572(16)	2.114(5) (M = Li)	2.442 (av.)	2.416 (av.)	2.422
Sc1-C_{alkyl}	2.247 (av.)	2.245 (av.)	2.282 (av.)	-	2.417(6)
M-O	2.0821(11)	1.904(5) (M = Li)	1.945 (av.)	1.879(3)	1.918(4)
C1-Sc1-C11	-	-	166.4 (av.)	174.48(16)	177.2(2)
O1-Sc1-O2	-	-	131.8 (av.)	127.9(2)	120.96(19)

Table 1. Selected bond lengths (Å) and angles (º) of a) $[(L)ScR_2]_2$, b) $(L^{Li})ScR_3$, c) $(L)_2ScR$, d) $(L)_2ScCl$, and e) $(L)_2Sc(C_6F_5)$.

Single crystals of $[(L)M R_2]_2$ (M = Sc or Y, R = CH_2SiMe_3) were grown from toluene solutions at -20ºC. The displacement ellipsoid plot when M = Sc is shown in Figure 1a). The molecular structure of $[(L)MR_2]_2$ (M = Sc or Y) is dimeric in the solid state with the alkoxy groups bridging the metal centers to form an M_2O_2 core which is centered over a crystallographic inversion centre. Each metal centre is five-coordinate, in a distorted trigonal bipyramidal geometry where the silylalkyl groups and one alkoxy bridging group define the equatorial plane. The L ligand is not parallel with the C_2O_2 plane but pitched away from the plane defined by the C_2O_2 core by approximately 28º. The Sc-$C_{carbene}$ (2.4572(16) Å) and Sc-$C_{alkyl,\ average}$ (2.247 Å) bond lengths are comparable to those previously reported complexes: Sc-$C_{carbene}$ = 2.350(3) Å and Sc-$C_{alkyl,\ average}$ = 2.209 Å in $(L)ScR_2$ (L = $IndCH_2CH_2$(1-C{NCHCHNMes}),[17] Sc-$C_{carbene}$ = 2.343(4) Å and Sc-$C_{alkyl,\ average}$ = 2.201 Å in $(L)ScR_2$ (L = $FluCH_2CH_2$(1-C{NCHCHNMes})).[42]

Crystals of $(L^{Li})ScR_3$ were grown from a toluene solution at -20 ºC. The displacement ellipsoid plot is shown in Figure 1b). Lithium NHC complexes remain rare.[43] The molecular structure of $(L^{Li})ScR_3$ contains the shortest reported Li-$C_{carbene}$ distance (2.114(5) Å) reported to date. Existing examples range from 2.124(4) Å in $[Li(L)]_2$ (L = ^{t}BuNCH$_2$CH$_2$(1-C{NCHCHN^{t}Bu}))[44] to 2.237(3) Å in $[Li(L)(C{\equiv}C^tBu)]_4$ (L = (1-C{NMeCMe}$_2$)).[45] The Li-$C_{carbene}$-centroid$_{NHC}$ angle is approaching linearity (166.5º) and so there is no severe distortion. The Li-$C_{carbene}$ distance is far shorter than the Sc-$C_{carbene}$ distance in $[(L)ScR_2]_2$ (2.4572(16) Å) and much shorter than expected based on the differences in ionic radii ($Li^{I,\ 6C.N.}$ = 0.76 Å, $Sc^{III,\ 6C.N.}$ = 0.745 Å).[46]

The coordination geometry at the scandium centre is distorted tetrahedral, with the Sc-$C_{alkyl,\ average}$ bond length (2.245 Å) very similar to that in $[(L)ScR_2]_2$ (2.247 Å). The Li^I ion forms part of a six-membered metallacyclic ring where five of the atoms (O1-Li1-C1-N1-C8) are, unusually, virtually co-planar and Li1 is in a distorted trigonal coordination environment, sitting 0.471 Å above the plane defined by O1-O2-C1.

Crystals of $(L)_2ScR$ were grown from a toluene solution at -30 ºC. The displacement ellipsoid plot is shown in Figure 1c). $(L)_2ScR$ crystallized with four molecules in each asymmetric unit of the unit cell. It is noted that one molecule (labeled C) was largely disordered. Comparable to all of the $(L)_2ScX$ molecular structures discussed here, the scandium cation is in a distorted trigonal bipyramidal environment with the alkoxide and chloride groups defining the equatorial plane. The bond lengths and angles are comparable to those previously reported scandium alkyl complexes.

Crystals of $(L)_2ScCl$ were grown from C_6D_6 at room temperature from the reaction mixture of $(L)_2ScR$ and Me_3SiCl. The displacement ellipsoid plot is shown in Figure 1d). The scandium centre is in a distorted trigonal bipyramidal coordination environment (C1-Sc1-C11 = 174.48(16)º, C1-Sc1-Cl1 = 90.23(11)º, O1-Sc1-Cl1 = 115.12(15)º) with the alkoxide and chloride groups defining the equatorial plane. There is a significant asymmetry to the coordination of the N-heterocyclic ring to the metal ion (N1-C1-Sc1 = 115.1(3)º, N2-C1-Sc1 = 136.6(3)º), with the *N*-Dipp groups being forced backwards in order to minimize unfavorable interactions. A C_2 axis is present through the Sc1-Cl1 bond.

Crystals of $(L)_2Sc(C_6F_5)$ were grown from a saturated toluene solution at -20 ºC, but the quality of the data is not very good. The displacement ellipsoid plot is shown in Figure 1e). $(L)_2Sc(C_6F_5)$ crystallized with two molecules in each asymmetric unit of the unit cell and, since both have very similar metrical parameters, only one is discussed here. The metal ion has a trigonal bipyramidal coordination geometry with the carbene donors as axial groups (O1-Sc1-O2 = 120.96(19)º and C1-Sc-C11 = 177.8(2)º), the N-heterocyclic rings being near co-planar (interplane angle defined by N1-C1-N2 and N3-C11-N4 = 8.73 Å) and the bulky *N*-Dipp groups opposite to each other in order to minimize unfavorable interactions. The Sc-$C_{carbene}$ bond length (2.412(5) Å) is comparable to that in $(L)_2ScI$ (2.431(2) Å). The Sc-C_{aryl} bond length in $(L)_2Sc(C_6F_5)$ (2.412(5) Å) is long. Comparison with $(L)Y(C_6F_5)_2(thf)$ (L = 1-NPh-2-CHNPh-C_6H_4) (2.492(3) Å) confirms this even when taking into account with 0.155 Å difference in ionic radii of Sc^{III} and Y^{III}.[46] The Sc···$F_{average}$ bond distance of 3.53 Å is also long (outside the combined van der Waals' radii of 3.47 Å) and there is no significant asymmetry in the coordination of the C_6F_5 group to the scandium centre (C48-C47-Sc1 = 125.0(4) Å and C52-C47-Sc1 = 123.89(4) Å) to indicate the presence of any stabilizing Sc···F interactions (see SI for discussion of Sc···F interactions in $[(L)Sc(R)(C_6F_5)]_2$).

Conclusions

The addition of E-X, where E is a functional group such as silyl, phosphinyl or stannyl and X is a halide, across the metal-carbene bond in scandium and yttrium alkyl complexes with tethered, bidentate NHC ligands results in the formation of unstable metal 'ate' complexes. The displaced NHC

group binds E the heteroatom functional group, and the halide X binds to the metal. The addition reaction appears to be driven by the formation of a strong M-X bond and the use of a polar substrate. Subsequent thermolysis is facile for these organolanthanide complexes, and in each case allows the formation of the heteroatom-functionalized hydrocarbon. The remaining lanthanide halide metal product can be recycled back to the alkyl complex by standard salt elimination routes. This chemistry is particularly straightforward for the bis(ligand) complexes presumably due to an increased level of steric protection afforded to the metal complexes.

The combination of Lewis acidic metal cation and nucleophilic carbene is strong enough to cleave the C-I bond in iodofluoroarenes offering a clean route to metallofluorobenzenes. The combination is not sufficiently reactive to cleave even the weakest carbon halogen bonds by addition across the metal-carbene bond, but the lithium carbene 'ate' complexes are reactive enough to allow a new means for the formation of carbon-carbon bonds at a redox-innocent organometallic such as found in Group 3 and lanthanide chemistry. This new type of C-element bond forming reaction might be of particular use to a metal complex with no access to two-electron redox chemistry.

The analogy between this Lewis-acid/NHC reactivity to frustrated Lewis pairs, and also catalytic reactions that combine NHCs with Lewis acidic metal catalysts[47] suggests that tuning of these systems may allow for a variety of other small molecules to be activated and incorporated into organo-rare earth metal chemistry. The successful formation of C-heteroatom bonds suggests that asymmetric versions of the ligand, readily available from chiral epoxides and primary amines,[48] might allow asymmetric carbon-element bonds to be formed. Work is in progress to develop asymmetric routes to silanes and phosphines, and to develop the potential for a relevant catalytic cycle for the formation of carbon-carbon and carbon-heteroatom bonds.

Experimental Details

1. General Details

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of dinitrogen. Protio solvents were degassed by sparging with dinitrogen, dried by passing through a column of activated sieves and stored over potassium mirrors (hexanes, toluene, benzene) or activated 4 Å molecular sieves (thf). Deuterated solvents were dried over potassium (d_6-benzene, d_8-thf), distilled under reduced pressure, freeze-pump-thaw degassed three times prior to use.

^{1}H NMR spectra were recorded at 298 K, unless otherwise stated, on Bruker AVA 400, AVA 500 or AVA 600 spectrometers and ^{13}C{^{1}H} or ^{13}C spectra on the same spectrometers at operating frequencies of 100, 125 and 150 MHz respectively. Two dimensional ^{1}H-^{1}H and ^{13}C-^{1}H correlation

experiments were used, when necessary, to confirm ^{1}H and ^{13}C assignments. All NMR spectra were referenced internally to residual protio solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz. Mass spectra were recorded by the mass spectrometry service of the University of Edinburgh's School of Chemistry. Elemental analyses were carried out at London Metropolitan University.

2. Synthetic Details

$ScCl_3(thf)_3$, $YCl_3(thf)_{3.5}$, $Sc(CH_2SiMe_3)_3(thf)_2$, $Y(CH_2SiMe_3)_3(thf)_2$, $Sc(CH_2CMe_3)_3(thf)_{1.5}$, $Y\{CH(SiMe_3)_2\}_3(thf)_2$,[49] and HL[50] were prepared with reference to published methods. Ph_3CCl was recrystallized from toluene and washed with hexanes, TMSCl was distilled under reduced pressure, TMSI was distilled under reduced pressure and stored in the absence of light, BnBr was dried over activated alumina and distilled under reduced pressure and then stored in the dark, Ph_3SnCl was sublimed (10^{-4} Torr, 90 ºC) and Ph_2PCl was distilled under reduced pressure (10^{-1} Torr, 120 ºC) prior to use. All other reagents were purchased and used without further purification.

2.1. Synthesis of mono(L) complexes

2.1.1. Synthesis of (L)Sc(CH_2SiMe_3)$_2$

a. At 0 ºC, to a slurry of $Sc(CH_2SiMe_3)_3(thf)_2$ (1.1 g, 2.4 mmol) in hexanes (15 mL) was added a solution of HL (0.72 g, 2.4 mmol) in hexanes (10 mL). The reaction mixture was stirred for 3 h during which time a white precipitate formed. The precipitate was collected by filtration and dried *in vacuo* to afford (L)Sc(CH_2SiMe_3)$_2$ as a white powder. Storage at room temperature in the solid state or in solution led to decomposition over a period of 24 h. Yield: 0.77 g (62 %). Diffraction quality crystals were grown from a toluene solution at -20 ºC. ^{1}H NMR (C_6D_6, 500 MHz): 7.26 (1 H, t, $^{3}J_{HH}$ = 8 Hz, 4-C_6H_3), 7.16 (2 H, d, $^{3}J_{HH}$ = 8 Hz, 3,5-C_6H_3), 3.33 – 3.20 (2 H, br m, $\underline{H}CMe_2$), 3.25 and 2.92 (2 H each, t, $^{3}J_{HH}$ = 11 Hz, NCH_2CH_2N), 2.17 (2 H, s, $OCMe_2C\underline{H}_2$), 1.61 (6 H, s, CMe_2), 1.53 and 1.14 (6 H each, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.21 (9 H, s, SiMe), -0.21 (2 H, br. s, $C\underline{H}_2SiMe_3$) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz): 147.0 (1-C_6H_3), 137.3 (2,6-C_6H_3), 129.5 (4-C_6H_3), 125.2 (3,5-C_6H_3), 75.9 ($\underline{C}Me_2$), 54.3 and 52.0 (NCH_2CH_2N), 28.3 ($H\underline{C}Me_2$), 26.4 and 24.1 ($HC\underline{Me}_2$), 4.6 (SiMe) ppm. The NCN, $C\underline{Me}_2$ and $CH_2Si\underline{Me}_3$ resonances could not be located. Anal. Found (calcd for $C_{27}H_{51}N_2OScSi_2$): C, 62.18 (62.26); H, 8.77 (9.87); N, 5.48 (5.38).

b. *in situ* preparation from $ScCl_3(thf)_3$: At -78 ºC, to a slurry of $ScCl_3(thf)_3$ (0.28 g, 0.77 mmol) in hexanes/thf (15 mL/20 mL) was added dropwise a solution of $LiCH_2SiMe_3$ (0.29 g, 3.1 mmol) in hexanes (20 mL) to afford a clear, colorless solution. The reaction mixture was stirred at 0 ºC for 2 h

and then a slurry of $[H_2L]Cl$ (0.26 g, 0.77 mmol) in thf (20 mL) was added in one portion to afford a clear, colorless solution. The reaction mixture was stirred for 2 h and then the volatiles were removed *in vacuo* to give a white solid. Extraction into cold (0 ºC) toluene (2 x 10 mL) afforded a clear, pale yellow solution. The volatiles were removed *in vacuo* afford a white solid. The synthesis of $(L)Sc(CH_2SiMe_3)_2$ was confirmed by ^1H NMR spectroscopy. This route was not as clean as the simple protonolysis reaction and required recrystallisation for purification.

2.1.2. Synthesis of $(L)Y(CH_2SiMe_3)_2$

At 0 ºC, to a solution of $Y(CH_2SiMe_3)_3(thf)_2$ (0.55 g, 1.1 mmol) in hexanes (15 mL) was added dropwise a solution of HL (0.34, 1.1 mmol) in hexanes (10 mL) to afford a clear, pale yellow solution. The reaction mixture was stirred for 1 h to yield a white precipitate which was collected by filtration, washed with hexanes (3 x 5 mL) and dried *in vacuo* to afford $(L)Y(CH_2SiMe_3)_2$ as a white powder. Storage at room temperature, both in the solid state and in solution led to decomposition over the course of 24 h. Yield: 0.32 g (51 %). Diffraction quality crystals were grown from a saturated toluene solution at -20 ºC. ^1H NMR (C_6D_6, 500 MHz): 7.27 - 7.02 (3 H, overlapping m, 4-C_6H_3 and 3,5-C_6H_3), 3.20 (2 H, t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 3.14 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 2.89 (2 H, t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 2.11 (2 H, s, $OCMe_2C\underline{H}_2$), 1.56 (6 H, s, CMe_2), 1.50 and 1.15 (6 H each, d, $^3J_{HH}$ = 7, $HC\underline{Me}_2$), 0.26 (18 H, s, SiMe), -0.65 - -0.96 (2 H, br. m, $C\underline{H}_2SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): 215.4 (d, $^1J_{YC}$ = 30 Hz, NCN), 146.7 (1-C_6H_3), 136.8 (2,6-C_6H_3), 129.7 (4-C_6H_3) 125.0 (3,5-C_6H_3), 74.5 ($\underline{C}Me_2$), 60.8 ($OCMe_2\underline{C}H_2$), 54.0 and 52.4 (NCH_2CH_2N), 37.6 ($^1J_{YC}$ = 38 Hz, $\underline{C}H_2SiMe_3$), 30.5 (CMe_2), 28.4 ($H\underline{C}Me_2$), 25.8 and 24.8 ($HC\underline{Me}_2$), 4.8 (SiMe). Anal. Found (calcd for $C_{27}H_{51}N_2OSi_2Y$): C, 57.35 (57.42); H, 8.98 (9.10); N 5.03 (4.96).

2.2. Synthesis of mono(L) ate complexes

2.2.1. Synthesis of $\{1\text{-}Li(thf)C(NDippCH_2CH_2N)\}CH_2CMe_2O)Sc(CH_2SiMe_3)_3$

To a slurry of $ScCl_3(thf)_3$ (1.0 g, 2.8 mmol) in thf (40 mL) at -78 ºC was added dropwise a solution of $LiCH_2SiMe_3$ (1.1 g, 11 mmol). The reaction mixture was allowed to warm to 0 ºC and stirred for 2 h. To the reaction mixture was added a solution of HL (0.85 g, 2.8 mmol) and it was then stirred for a further 2 h. The volatiles were removed *in vacuo* to yield a white powder. Extraction into toluene (3 x 15 mL) and removal of the volatiles under reduced pressure gave a white powder which was washed with hexanes (3 x 15 mL) and dried once more to afford $\{1\text{-}Li(thf)C(NDippCH_2CH_2N)\}CH_2CMe_2O)Sc(CH_2SiMe_3)_3$ as a white solid. Yield: 1.45 g (75 %). ^1H NMR (C_6D_6, 600 MHz): 7.08 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 6.96 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 3.13

(2 H, t, $^3J_{HH}$ = 6 Hz, C_2H_4O), 3.12 (2 H, s, $OCMe_2\underline{C}H_2$), 2.85 (2 H, t, $^3J_{HH}$ = 10 Hz, NCH_2CH_2N), 2.90 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 3.05 (2 H, t, $^3J_{HH}$ = 10 Hz, NCH_2CH_2N), 1,51 (6 H, s, CMe_2), 1.21 (2 H, t, $^3J_{HH}$ = 6 Hz, C_2H_4O), 1.15 and 1.09 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.42 (27 H, s, SiMe), -0.16 (6 H, s, $C\underline{H}_2SiMe_3$) ppm.$^{13}C\{^1H\}$ NMR (C_6D_6, 150 MHz): 221.1 (NCN), 147.6 and 147.4 (2,6-C_6H_3), 138.2 and 137.8 (1-C_6H_3), 128.9 and 128.8 (4-C_6H_3), 124.3 (3,5-C_6H_3), 74.0 ($\underline{C}Me_2$), 68.0 (C_2H_4O), 62.2 ($OCMe_2\underline{C}H_2$), 52.8 and 51.7 (NCH_2CH_2N), 35.4 ($\underline{C}H_2SiMe_3$), 30.9 ($C\underline{Me}_2$), 28.4 and 28.3 ($H\underline{C}Me_2$), 25.3 (C_2H_4O), 24.8 and 24.7 ($HC\underline{Me}_2$), 4.39 (SiMe) ppm. Anal. Found (calcd for $C_{35}H_{70}LiN_2O_2ScSi_3$): C, 60.12 (61.18); 10.09 (10.27); N, 4.45 (4.66). This analysis was performed on a sample of powdered single crystals. The low C percentage is noted and presumed due to the formation of metal carbide in the analysis.

2.2.2. Synthesis of {1-$Me_3SiC(NDippCH_2CH_2N)$}$CH_2CMe_2O)Sc(CH_2SiMe_3)_3$

At 0 ºC, to a solution of {1-Li(thf)C(NDippCH_2CH_2N)}$CH_2CMe_2O)Sc(CH_2SiMe_3)_3$ (0.34 g, 0.51 mmol) in toluene (5 mL) was added a solution of Me_3SiCl (64 µL, 0.51 mmol) in toluene (5 mL). The reaction mixture was stirred for 2 h. The volatiles were removed *in vacuo* to afford {1-$Me_3SiC(NDippCH_2CH_2N)$}$CH_2CMe_2O)Sc(CH_2SiMe_3)_3$ as a colorless powder. Storage at room temperature in solution resulted in further elimination reactivity or decomposition in the solid state. Yield: 0.27 g (78 %). ^1H NMR (C_6D_6, 500 MHz): 6.99 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 6.75 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 4.58 and 3.35 (2 H each, t, $^3J_{HH}$ = 12 Hz, NCH_2CH_2N), 2.46 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 3.30 (2 H, s, $OCMe_2C\underline{H}_2$), 1.52 (6 H, s, CMe_2), 0.93 (12 H, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.58 (27 H, s, $CH_2Si\underline{Me}_3$), 0.16 (6 H, br. s, $C\underline{H}_2SiMe_3$), -0.43 (9 H, s, $CSiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): ppm. 174.8 (NCN), 146.3(1-C_6H_3), 132.4 (2,6-C_6H_3), 131.3(4-C_6H_3), 125.2 (3,5-C_6H_3), 73.02 ($\underline{C}Me_2$), 64.2 ($OCMe_2\underline{C}H_2$), 54.7 and 51.5 (NCH_2CH_2N), 31.5 ($C\underline{Me}_2$), 28.5 ($H\underline{C}Me_2$), 25.6 and 23.3 ($HC\underline{Me}_2$), 4.91 ($CH_2Si\underline{Me}_3$ and $\underline{C}H_2SiMe_3$),1.48 ($CSi\underline{Me}_3$) ppm. Anal. Found (calcd for $C_{34}H_{71}N_2OScSi_4$): C, 59.89 (59.94); H, 10.41 (10.50); N, 4.14 (4.11).

2.3. Synthesis of bis(L) complexes

2.3.1. Synthesis of $(L)_2Sc(CH_2SiMe_3)$

a. From $Sc(CH_2SiMe_3)_3(thf)_2$: At 0 ºC, to a clear, colorless solution of $Sc(CH_2SiMe_3)_3(thf)_2$ (0.86 g, 1.9 mmol) in hexanes (20 mL) was added a solution of HL (1.2 g, 3.8 mmol) in hexanes (10 mL). The reaction mixture was allowed to warm to room temperature and was stirred at room temperature for 1.5 h at room temperature to afford a clear, colorless solution. The volatiles were removed under reduced pressure to afford $(L)_2Sc(CH_2SiMe_3)$ as a white solid. Yield: 1.1 g (81 %). Diffraction quality

crystals were grown from a hexanes solution at -20 ºC. ^{1}H NMR (C_6D_6, 500 MHz): 7.27 (2 H, t, $^{3}J_{HH}$ = 8 Hz, 4-C_6H_3), 7.26 (4 H, d , $^{3}J_{HH}$ = 8 Hz, 3,5-C_6H_3), 3.74 (2 H, d, $^{3}J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 3.32 (2 H, m, $\underline{H}CMe_2$), 3.25 – 2.28 (10 H, overlapping m, NCH_2CH_2N and $\underline{H}CMe_2$), 2.56 (2 H, d, $^{3}J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 1.58 1.51 1.21 and 1.16 (6 H each, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$) 0.87 and 0.60 (6 H each, s, CMe_2), 0.37 (9 H, s, $CH_2Si\underline{Me}_3$), -0.33 and -0.72 (1 H each, d, $^{2}J_{HH}$ = 11 Hz, $C\underline{H}_2SiMe_3$) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz): 147.8 and 147.1 (2,6-C_6H_3), 138.4 (1-C_6H_3), 128.4 (4-C_6H_3), 124.02 (3,5-C_6H_3), 72.7 ($\underline{C}Me_2$) 62.41 ($OCMe_2\underline{C}H_2$), 53.3 and 52.7 ($H\underline{C}Me_2$ and NCH_2CH_2N), 30.2 ($C\underline{Me}_2$), 28.7 ($\underline{C}H_2SiMe_3$), 28.3 ($C\underline{Me}_2$), 27.6 25.9 25.3 and 25.1 ($HC\underline{Me}_2$), 4.7 (SiMe) ppm. The NCN resonance could not be located. Anal. Found (calcd for $C_{42}H_{69}N_4O_2ScSi$): C, 68.50 (68.63); H, 9.26 (9.46); N, 7.74 (7.62).

b. From $(L)_2ScCl$: $(L)_2ScCl$ (0.014 g, 0.020 mmol) and $LiCH_2SiMe_3$ (0.0019 g, 0.020 mmol) were combined in C_6D_6 in a J-Young teflon valve NMR tube. The reaction mixture was heated to 80 ºC for 12 h. The formation of $(L)_2Sc(CH_2SiMe_3)$ was confirmed by ^{1}H NMR spectroscopy.

2.3.2. Synthesis of $(L)_2Sc(CH_2CMe_3)$

At 0 ºC, to a clear, colorless solution of $Sc(CH_2CMe_3)_3(thf)_{0.65}$ (0.10 g, 0.34 mmol) in hexanes (5 mL) was added a solution of HL (0.15 g, 0.51 mmol) in hexanes (5 mL). The reaction mixture was allowed to warm to room temperature and was stirred at room temperature for 1.5 h at room temperature to afford a clear, colorless solution. The volatiles were removed under reduced pressure to afford $(L)_2Sc(CH_2CMe_3)$ as a white solid. Yield: 0.11 g (47 %). Diffraction quality crystals were grown from a hexanes solution at -20 ºC. ^{1}H NMR (C_6D_6, 500 MHz): 7.30 (2 H, t, $^{3}J_{HH}$ = 8 Hz, 4-C_6H_3), 7.18 (4 H, m, 2,6-C_6H_3) , 3.92 (2 H, d, $^{3}J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 3.46 (2 H, sept, $^{3}J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 3.27 (2 H, m, NCH_2CH_2N), 3.11 – 2.87 (6 H, overlapping m, $\underline{H}CMe_2$ and NCH_2CH_2N), 2.64 (2 H, d, $^{3}J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 1.62 and 1.52 (6 H each, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 1.41 (9 H, s, CMe_3), 1.22 and 1.16 (6 H each, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.91 and 0.67 (6 H each, s, CMe_2), 0.50 and 0.37 (1 H each, d, $^{1}J_{HH}$ = 12 Hz, $C\underline{H}_2CMe_3$) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 500 MHz): 147.9 and 147.1 (2,6-C_6H_3), 138.6 (1-C_6H_3), 124.0 (3,5-C_6H_3), 72.5 ($\underline{C}Me_2$), 62.3 ($OCMe_2\underline{C}H_2$), 53.3 ad 52.8 (NCH_2CH_2N), 36.9 (^{t}Bu), 31.6 ($C\underline{Me}_2$), 28.7 and 28.2 ($H\underline{C}Me_2$), 27.8 ($C\underline{Me}_2$), 26.0 25.8 25.5 and 25.1 ($HC\underline{Me}_2$) ppm. The resonance for the 4-C_6H_3 C was obscured by the C_6D_6 resonance and the NCN and $C\underline{H}_2CMe_3$ resonances could not be located. Anal. Found (calcd for $C_{43}H_{69}N_4O_2Sc$): C, 71.74 (71.83); H, 9.75 (9.67); N, 7.61 (7.79).

2.3.3. Synthesis of $(L)_2Y(CH_2SiMe_3)$

To a clear, colorless solution of $Y(CH_2SiMe_3)_3(thf)_2$ (0.27 g, 0.55 mmol) in hexanes (10 mL) was added a solution of HL (0.33 g, 1.11 mmol) in hexanes (5 mL) to afford a pale yellow solution. The reaction mixture was stirred for 12 h at room temperature and then the volatiles were removed under reduced pressure to yield a pale yellow solid which was washed with hexanes (3 x 5 mL) and dried under reduced pressure to afford $(L)_2Y(CH_2SiMe_3)$ as a white solid. Yield: 0.14 g (33 %). ^{1}H NMR (C_6D_6, 600 MHz): 7.29 (2 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3) 7.17 (4 H, m, 3,5-C_6H_3), 3.63 (2 H, d, $^3J_{HH}$ = 14 Hz, $OCMe_2C\underline{H}_2$), 3.38 – 2.85 (12 H, overlapping m, NCH_2CH_2N and $\underline{H}CMe_2$), 2.67 (2 H, d, $^3J_{HH}$ = 14 Hz, $OCMe_2C\underline{H}_2$), 1.57 1.49 and 1.19 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.87 and 0.79 (6 H each, s, CMe_2), 0.41 (9 H, s, SiMe), -0.48 and -1.04 (1 H each, dd, $^1J_{HH}$ = 11 Hz, $^1J_{YH}$ = 3 Hz, $C\underline{H}_2SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): 217.9 (d, $^1J_{YC}$ = 33 Hz, NCN), 147.6 and 147.2 (2,6-C_6H_3), 137.7 (1-C_6H_3), 128.6 (4-C_6H_3), 124.1 and 124.0 (2,6-C_6H_3), 67.9 and 63.2 ($OCMe_2\underline{C}H_2$), 53.2 and 53.0 (NCH_2CH_2N), 31.2 and 28.7 ($C\underline{Me}_2$), 28.3 and 28.0 ($H\underline{C}Me_2$), 25.9 25.6 25.1 and 25.0 ($HC\underline{Me}_2$) 5.0 (SiMe) ppm. The $\underline{C}H_2SiMe_3$ resonance could not be located. Satisfactory elemental analysis was not obtained from powdered single crystals and the compound decomposes readily at room temperature.

2.4. Addition/Elimination reactions of bis(L) complexes to form carbon-silicon bonds

2.4.1. Reaction of $(L)_2Sc(CH_2SiMe_3)$ with E-X to form C-Si bonded products

2.4.1.1. Reaction of $(L)_2Sc(CH_2SiMe_3)$ with Me_3Si-Cl to form a C-Si bond and $(L)_2ScCl$

a. Preparative scale: $(L)_2Sc(CH_2SiMe_3)$ (0.17 g, 0.23 mmol) and Me_3SiCl (29 μL, 0.23 mmol) were combined in C_6D_6 (1 mL) in a J-Young teflon valve NMR tube to afford a clear, colorless solution. After 5 days, colorless crystals had formed and these were isolated by filtration, washed with hexanes (3 x 2 mL) and dried *in vacuo* to afford $(L)_2ScCl$ as a colorless solid. Yield: 0.071 g (45 %). Diffraction quality crystals were grown from a saturated C_6D_6 solution. ^{1}H NMR (C_6D_6, 500 MHz): 7.25 (2 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 7.19 and 7.14 (2 H each, dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 3,5-C_6H_3), 3.69 (2 H, d, $^3J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 3.59 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 3.25 – 3.19 (2 H, m, NCH_2CH_2N), 3.11 – 3.03 (4 H, overlapping m, $\underline{H}CMe_2$ and NCH_2CH_2N), 2.92 - 2.82 (4 H, m, NCH_2CH_2N), 2.49 (2 H, d, $^3J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 1.72 1.60 1.21 and 1.21 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 0.98 and 0.50 (CMe_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): ppm. 215.2 (NCN), 147.8 147.6 and 129.3 (1,2,6-C_6H_3), 128.6 (4-C_6H_3), 124.3 and 124.1 (3,5-C_6H_3), 73.3 ($\underline{C}Me_2$), 62.3 ($OCMe_2\underline{C}H_2$), 52.3 and 52.6 (NCH_2NCH_2), 29.4 ($C\underline{Me}_2$), 28.8 and 28.2 ($H\underline{C}Me_2$), 27.2 ($C\underline{Me}_2$), 25.8 25.4 and 25.0 ($HC\underline{Me}_2$) ppm. Anal. Found (calcd for $C_{38}H_{58}ClN_4O_2Sc$): C, 67.16 (66.79); H, 8.91 (8.56); N, 7.85 (8.20).

b. NMR tube scale: To a solution of $(L)_2Sc(CH_2SiMe_3)$ (0.024 g, 0.032 mmol) in C_6D_6 (1 mL) in a J-Young teflon valve NMR tube was added Me_3SiCl (4.2 μL, 0.032 mmol) to afford a clear, colorless solution. Over the course of 5 days the reaction was monitored by ^1H NMR spectroscopy and the formation of $(L)_2ScCl$ and $Me_3SiCH_2SiMe_3$ was observed.

2.4.1.2. Reaction of $(L)_2Sc(CH_2SiMe_3)$ with E-X to form a C-Si bond and $(L)_2ScI$

NMR tube scale Me_3SiI: To a solution of $(L)_2Sc(CH_2SiMe_3)$ (0.066 g, 0.090 mmol) in C_6D_6 (1 mL) in a J-Young teflon valve NMR tube was added Me_3SiI (12.8 μL, 0.090 mmol) to afford a clear, colorless solution. Over the course of 5 days the reaction was monitored by ^1H NMR spectroscopy and the formation of $(L)_2ScI$ was observed. The volatiles were distilled off and were shown to contain $Me_3SiCH_2SiMe_3$ by ^1H NMR spectroscopy.

2.4.1.3. Reaction of $(L)_2Sc(CH_2CMe_3)$ with E-X to form C-Si bonded products

Me_3SiCl: To a solution of $(L)_2Sc(CH_2CMe_3)$ (0.012 g, 0.017 mmol) in C_6D_6 (1 mL) in a J-Young teflon valve NMR tube was added Me_3SiCl (2.1 μL, 0.017 mmol) to afford a clear, colorless solution. Over the course of 10 days the reaction was monitored by ^1H NMR spectroscopy and the formation of $(L)_2ScCl$ and $Me_3SiCH_2CMe_3$. ^1H NMR: (C_6D_6, 400 MHz, 298 K): 1.26 (9 H, s, CMe_3), 0.14 (9 H, s, SiMe), 0.07 (2 H, s, CH_2) ppm.

2.4.2. Thermolytic elimination reactions of mono(L) 'ate' complexes to form carbon-silicon and carbon-carbon bonds

2.4.2.1. Reaction of $\{1\text{-}Li(thf)C(NDippCH_2CH_2N)\}CH_2CMe_2O)Sc(CH_2SiMe_3)_3$ with E-X to give C-C bond formation

Ph_3CCl: To a solution of $\{1\text{-}Li(thf)C(NDippCH_2CH_2N)\}CH_2CMe_2O)Sc(CH_2SiMe_3)_3$ (0.11 g, 0.16 mmol) in toluene (2 mL) was added a solution of Ph_3CCl (0.045 g 0.16 mmol) in toluene (1 mL) to immediately afford a pale orange solution. The reaction mixture was allowed to stir for 1 h during which time a white precipitate formed. No NMR evidence for any intermediate was observed. The solution was filtered off and the precipitate was washed with toluene (3 x 1 mL). The combined washings were dried *in vacuo* to afford an orange solid. ^1H NMR spectral analysis showed this to be a combination of $(L)Sc(CH_2SiMe_3)_2$ and $Ph_3CCH_2SiMe_3$. EI-MS: *m/z*: 330.2 $[Ph_3CCH_2SiMe_3]^+$ (25 %), 315.2 $[Ph_3CCH_2SiMe_3\text{-}Me]^+$ (6 %), 243.1 $[Ph_3CCH_2SiMe_3\text{-}CH_2SiMe_3]^+$ (100 %).

2.4.2.2. Thermolysis of {1-$Me_3SiC(NDippCH_2CH_2N)$}$CH_2CMe_2O)Sc(CH_2SiMe_3)_3$ to give C-Si bond formation

{1-$Me_3SiC(NDippCH_2CH_2N)$}$CH_2CMe_2O)Sc(CH_2SiMe_3)_3$ (0.021 g, 0.031 mmol) was dissolved in C_6D_6 (1 mL) in a J-Young teflon valve NMR tube. The reaction mixture was kept at room temperature for 2 h, after which time the ^{1}H NMR spectrum contained resonances for $Me_3SiCH_2SiMe_3$, $(L)Sc(CH_2SiMe_3)_2$ (~ 0.9 equivalents) and $(L)_2Sc(CH_2SiMe_3)$ (~ 0.1 equivalents).

2.4.3. Addition reactions of bis(L)M complexes with E-X to form other carbon-heteroatom bonded products

2.4.3.1. C-P: Reaction of $(L)_2Sc(CH_2SiMe_3)$ with Ph_2PCl to form a C-P bond and $(L)_2ScCl$

Ph_2PCl: To a solution of $(L)_2Sc(CH_2SiMe_3)$ (0.051 g, 0.069 mmol) in C_6D_6 (1 mL) in a J-Young teflon valve NMR tube was added Ph_2PCl (12.3 µL, 0.069 mmol) to afford a clear, colorless solution. Over the course of 5 days the reaction was monitored by ^{1}H NMR spectroscopy and the formation of $(L)_2ScCl$ and $Ph_2PCH_2SiMe_3$ in 95 % yield was observed. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): 7.45 (12 H, m,-C_6H_4), 0.36 ($C\underline{H}_2SiMe_3$) ppm. EI-MS: *m/z*: 272.1 $[Ph_2PCH_2SiMe_3]^+$ (100 %).

2.4.3.2. C-Sn: Reaction of $(L)_2Sc(CH_2SiMe_3)$ with tris(hydrocarbyl) tin chlorides to form a C-Sn bond and $(L)_2ScCl$

a. ^{n}BuSnCl: To a solution of $(L)_2Sc(CH_2SiMe_3)$ (0.037 g, 0.051 mmol) in C_6D_6 (1 mL) in a J-Young teflon valve NMR tube was added $^nBu_3SnCl$ (14 µL, 0.051 mmol) to afford a clear, colorless solution. Over the course of 17 h the reaction was monitored by ^{1}H NMR spectroscopy and the formation of 1 equivalent of $(L)_2ScCl$ and 1 equivalent of $^nBu_3SnCH_2SiMe_3$ were observed. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): 1.67 (6 H, m, $(C\underline{H}_2)_3CH_3$), 1.49 (6 H, m, $(C\underline{H}_2)_3CH_3$)), 1.06 - 0.94 (36 H, overlapping m, 4-$(C\underline{H}_2)_3CH_3$ and 1-$(CH_2)_3C\underline{H}_3$), 0.24 (9 H, s, SiMe), -0.13 (2 H, s, $C\underline{H}_2SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): 29.7 ((2,3-$\underline{C}H_2)_3CH_3$), 27.9 (2,3-$(\underline{C}H_2)_3CH_3$), 14.0 (4-$(CH_2)_3\underline{C}H_3$), 10.7 (1-$(\underline{C}H_2)_3CH_3$, $^2J_{119SnC}$ = 162 Hz, $^2J_{117SnC}$ = 155 Hz), 1.9 (SiMe), -7.1 ($\underline{C}H_2SiMe_3$) ppm. EI-MS: *m/z*: 363.1 $[^nBu_3SnCH_2SiMe_3\text{-}Me]^+$ (5 %), 321.1 $[^nBu_3SnCH_2SiMe_3\text{-}^nBu]^+$ (100 %), 264.0 $[^nBu_3SnCH_2SiMe_3\text{-}2^nBu]^+$ (18 %), 207.0 $[^nBu_3SnCH_2SiMe_3\text{-}3^nBu]^+$ (66 %), 102.0 $[^nBu_3SnCH_2SiMe_3\text{-}^nBu_3Sn]^+$ (18 %).

b. Ph_3SnCl: $(L)_2Sc(CH_2SiMe_3)$ (0.019 g, 0.026 mmol) and Ph_3SnCl (0.010 g, 0.026 mmol) were combined in C_6D_6 (1 mL) in a J-Young teflon valve NMR tube. Over the course of 5 days the reaction

was monitored by ^{1}H NMR spectroscopy and the formation of $(L)_2ScCl$ and $Ph_3SnCH_2SiMe_3$ were observed. ^{1}H NMR (C_6D_6, 500 MHz. 298 K): 7.62 – 7.60 (3 H, overlapping m, C_6H_4), 7.21 – 7.13 (overlapping m, -C_6H_4), 0.36 (2 H, s, $\underline{C}H_2SiMe_3$), 0.01 (9 H, s, SiMe) ppm. Integration of the aromatic protons could not be performed accurately due to overlap with both the residual protio solvent and $(L)_2ScCl$ resonances. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz, 298 K): 137.3 and 128.7 (C_6H_4), 1.7 ($\underline{C}H_2SiMe_3$), -5.0 (SiMe) ppm. The remaining –C_6H_4 resonances are obscured by residual protio solvent and $(L)_2ScCl$ resonances. EI-MS: *m/z*: 423.1 $[Ph_3SnCH_2SiMe_3\text{-}Me]^+$ (10 %), 361.1 $[Ph_3SnCH_2SiMe_3\text{-}Ph]^+$ (14 %), 351.0 $[Ph_3SnCH_2SiMe_3\text{-}CH_2SiMe_3]^+$ (100 %).

2.4.3.3. C-I: Reaction of $(L)_2Sc(CH_2SiMe_3)$ with C_6F_5I to form a C-I bond and $(L)_2Sc(C_6F_5)$

a. Preparative scale $(L)_2Sc(CH_2SiMe_3)$ (0.15 g, 0.21 mmol) and C_6F_5I (27.6 µL, 0.21 mmol) were combined in C_6D_6 (1 mL) in a J-Young teflon valve NMR tube. Immediately, a colorless solid precipitated from the reaction mixture. This solid was washed with hexanes (3 x 1 mL) and the volatiles were removed *in vacuo* to afford $(L)_2Sc(C_6F_5)$ as a colorless solid. Yield: 0.15 g, (86 %). The organic product Me_3SiCH_2I, identified in the NMR tube reaction below, is unstable and decomposes over time in solution to a dark-colored material. Diffraction quality crystals of $(L)_2Sc(C_6F_5)$ were grown from a toluene solution at -20 ºC. ^{1}H NMR (C_6D_6, 500 MHz): 7.18 (2 H, t, $^{3}J_{HH}$ = 8 Hz, 4-C_6H_3), 7.13 and 6.92 (2 H each, dd, $^{3}J_{HH}$ = 8 Hz, $^{4}J_{HH}$ = 1 Hz, 2,6-C_6H_3) , 3.41 (2 H, d, $^{3}J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 3.25 – 2.91 (12 H, overlapping m, NCH_2CH_2N and $\underline{H}CMe_2$), 2.80 (2 H, d, $^{3}J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 1.63 (6 H, s, CMe_2), 1.60 and 1.16 (6 H each, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 1.11 (6 H, s, CMe_2), 0.99 and 0.94 (6 H each, d, $^{3}J_{HH}$ = 7 Hz, $HC\underline{Me}_2$) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz): 215.3 (NCN), 147.4 (3,5-C_6H_3), 146.9 (1-C_6H_3), 137.7 (4-C_6H_3), 124.4 and 123.7 (2,6-C_6H_3), 73.6 ($\underline{C}Me_2$), 62.5 ($OCMe_2\underline{C}H_2$), 53.0 and 52.8 (NCH_2CH_2N), 28.6 ($H\underline{C}Me_2$), 28.2 ($C\underline{Me}_2$), 28.1 ($H\underline{C}Me_2$), 26.0, 25.5, 24.9 and 23.1 ($HC\underline{Me}_2$) ppm. Anal. Found (calcd for $C_{44}H_{58}F_5N_4O_2Sc$): C, 64.70 (64.85); H, 7.07 (7.17); N, 6.78 (6.88).

b. NMR tube scale C_6F_5I: To a solution of $(L)_2Sc(CH_2SiMe_3)$ (0.012 g, 0.016 mmol) in C_6D_6 (1 mL) in a J-Young teflon valve NMR tube was added C_6F_5I (2.2 µL, 0.016 mmol) to afford a clear, colorless solution. ^{1}H NMR spectroscopy indicated the formation of $(L)_2Sc(C_6F_5)$ and Me_3SiCH_2I. Over the course of 24 h, the solution darkened in color and became dark pink. ^{1}H NMR spectroscopy showed the presence of $(L)_2Sc(C_6F_5)$ and Me_3SiCH_2I; the latter decomposes slowly in solution over time, darkening the solution.

3. Crystallographic Details

Crystals were mounted in an inert oil and X-ray crystallographic data were collected at 150 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), at 170 K on an Oxford Diffraction Xcalibur diffractometer using graphite monochromated Mo-Kα radiation, or at 100 K on an Oxford Diffraction Supernova diffractometer using mirror monochromated Cu-Kα radiation (λ = 1.54178 Å).[51] Using the WinGX suite of programs, all structures were solved using direct methods and refined using a full-matrix least square refinement on $|F|^2$ using SHELXL-97.[52] Unless otherwise stated, all non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed using a riding model and refined with fixed isotropic displacement parameters.[53] Complex neutral-atom scattering factors were used.[54] Refinement proceeded to give the residuals shown in Table 2.

Table 2. Selected experimental crystallographic data for a) $[(L)ScR_2]_2$, b) $(L^{Li})ScR_3$, c) $(L)_2ScR$, d) $(L)_2ScCl$, and e) $(L)_2Sc(C_6F_5)$.

Complex	$(L)ScR_2$	$(L^{Li})ScR_3$	$(L)_2ScR$	$(L)_2ScCl$	$(L)_2Sc(C_6F_5)$
			Crystal data		
Chemical formula	$C_{54}H_{102}N_4O_2Sc_2Si_4$	$C_{35}H_{70}LiN_2O_2ScSi_3$	$C_{42}H_{69}N_4O_2ScSi$	$C_{38}H_{58}ClN_4O_2Sc$	$C_{44}H_{58}F_5N_4O_2Sc$
M_r	1041.68	687.10	735.06	683.29	814.90
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Pbca$	Orthorhombic, $C222_1$	Monoclinic, Pn	Monoclinic, $C2/c$
Temperature (K)	100	150	150	150	100
a, b, c (Å)	9.5128 (1), 19.2311 (3), 19.6980 (3)	10.1400 (2), 22.3379 (5), 38.2117 (9)	32.2095 (4), 32.7595 (4), 34.3193 (5)	8.9058 (1), 11.9061 (2), 18.4358 (3)	38.7236 (16), 23.2484 (10), 20.6479 (8)
α, β, γ (°)	90, 97.888 (1), 90	90, 90, 90	90, 90, 90	90, 91.217 (1), 90	90, 110.141 (5), 90
V (Å^3)	3569.49 (9)	8655.2 (3)	36212.6 (8)	1954.37 (5)	17451.8 (12)
Z	2	8	8	2	16
Radiation type	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	2.53	0.28	0.22	0.29	1.95
Crystal size (mm)	0.11 × 0.08 × 0.04	0.55 × 0.50 × 0.45	0.19 × 0.15 × 0.11	0.21 × 0.19 × 0.15	0.17 × 0.17 × 0.07
			Data collection		
Diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer	Bruker *SMART APEX* CCD area detector diffractometer	Xcalibur, Eos diffractometer	Xcalibur, Eos diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer
Absorption correction	Multi-scan CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.55.[a]	Multi-scan *SADABS*	Multi-scan CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.34.44.[b]	Multi-scan CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.55.[a]	Multi-scan CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.55.[a]
T_{min}, T_{max}	0.944, 1.000	0.861, 0.884	0.964, 1.000	0.980, 1.000	0.572, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23809, 6985, 5376	98382, 10956, 9564	106897, 35881, 30576	22700, 8848, 6534	62621, 13666, 9691
R_{int}	0.059	0.064	0.026	0.020	0.059
			Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.091, 0.93	0.079, 0.161, 1.28	0.048, 0.117, 1.02	0.080, 0.227, 1.02	0.103, 0.388, 1.59
No. of reflections	6985	10956	35881	8848	13666
No. of parameters	310	412	1964	457	1033
No. of restraints	0	0	0	2	0
	$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 12.1028P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 31.7562P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1646P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, -0.24	0.51, -0.42	0.50, -0.84	1.34, -0.38	1.98, -1.14
Flack parameter[54]	–	–	-0.007 (14)	0.0(2)	–

a. 05-01-2010 CrysAlis171 .NET (compiled Jan 5 2010, 16:28:46). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

b. 25-10-2010 CrysAlis171 .NET (compiled Oct 25 2010, 18:11:34). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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